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RESEARCH ON LOW DENSITY
THERMAL INSULATION MATERIALS
FOR USE ABOVE 3000°F

Quarterly Status Report

Contract NASw-884

National Beryllia Corporation
Haskell, New Jersey

RESEARCH ON LOW-DENSITY THERMAL INSULATION MATERIALS FOR USE ABOVE 3000° F

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National Aeronautics and Space Administration

Quarterly Status Report
for the Period April 1 through June 30, 1964

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ABSTRACT

33121

Refractory composites of ceramic oxides and refractory metals are being developed and evaluated for use as high temperature thermal insulation. Several sources of high purity (less than 1000ppm impurities) zirconium dioxide powders are being evaluated with tungsten and molybdenum introduced in a variety of forms and concentrations.

A technical paper describing a high temperature radial heat flow thermal conductivity apparatus and a multiple gauge section technique, prepared for presentation at the International Conference on thermal conductivity, London, England, constitutes the major portion of this status report.

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(1) INTRODUCTION

This is the second quarterly report of Contract NASw-884 on the subject, "Research on Low Density Thermal Insulation Materials for Use above 3000°F". This program is a continuation of work performed on Contract NASr-99 which was conducted for seven quarters from April, 1962, through December, 1963.

1.1 Purpose of the Program

Low-density foamed ceramic thermal insulation rapidly loses efficiency above 2400°F due to the transfer of heat through the pores by thermal radiation. The purpose of this program is to study the reduction of this radiation or photon contribution to the thermal conductivity by the incorporation of a thermal radiation barrier phase into a low-density refractory structure. Mechanisms such as absorption and re-radiation by imbedded particles, scattering by incorporated phases and reflection by metallic foil radiation barriers are being investigated and evaluated.

1.2 Phases of the Program

The goals of this program are being achieved through the pursuit of the three phases described briefly below with details of the progress made during this quarter discussed in Section II.

Phase I - Technical Review

Review of previous high temperature heat transfer work, essentially completed during the first quarter, has been continued at a sufficient level of effort to keep abreast of the rapidly changing technology.

Phase II - Materials Formulation

The major effort of the program is concerned with the fabrication of low-density, low thermal conductivity materials. Light weight pure oxide ceramic matrices have been developed and impregnated with various volume percentages of potential radiation shielding phases introduced by a variety of techniques. Specimens of ceramic oxides whose thermal conductivity have been previously reported have also been prepared for calibration and equipment checkout purposes.

Phase III - Experimental Measurements

Evaluation of the thermal radiation barrier concept is being conducted in this phase of the program. A high temperature thermal conductivity test cell, capable of maintaining under steady conditions, specimen hot face temperatures of 4500°F and above has been fabricated and calibrated. Measurement of the apparent total conductivity of the ceramic foam composite test samples is in progress.

2 Discussion

This summary status report supplements the attached paper, "A Multiple Gauge Section Technique for the Measurement of Thermal Conductivity in Ceramic Foam Composites to 5000°F", to be presented July 16, 1964, at the International Thermal Conductivity Conference, sponsored by the National Physical Laboratory, Teddington, England. Many aspects of the measurement procedures modified from "normal practice" because of the microstructure of the specimens and the ranges of temperature and thermal conductivity encountered, are to be discussed so that the best possible data may be forthcoming from this program.

2.2 Phase II - Materials Formulations

2.2.1 Matrix Materials

Variation in the physical characteristics of several recent lots of high purity zirconium dioxide powders, as mentioned in the previous Quarterly Status Report, have caused significant variations in the properties of zirconia foams and of composites in which they form the matrix. This is particularly true at high temperatures on such properties as thermal shock resistance and strength. For this reason an alternate source of high purity powder with better apparent lot-to-lot uniformity has been evaluated. Fired foams of somewhat higher strength and density are obtained when "standard" processing procedures are used. Slight process modification has allowed fabrication of refractory foams of the desired density with improved high temperature properties and reproducibility. This type of foam, coded Zr 36, has been fabricated into conductivity specimens for measurement, however, results are not yet complete.

2.2.2 Composites

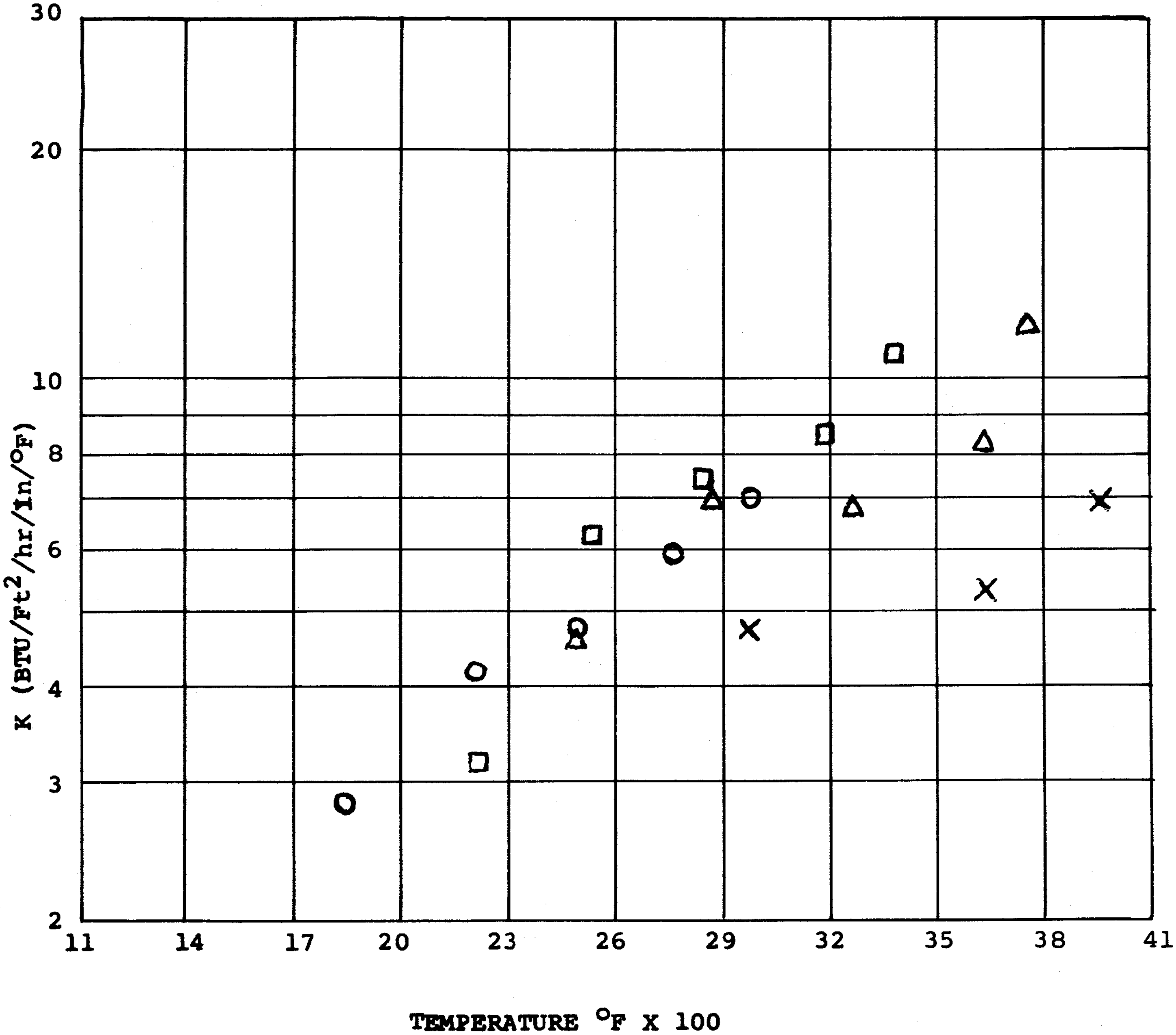
Zirconia foam specimens, similar to type Zr 36, have been prepared with molybdenum disilicide and tungsten metal additions. Results indicate minor modifications in processing are required to produce a material of comparable structure and density to the matrix foam. While composites of the desired structure have not yet been developed from the Zr 36 materials, no great difficulty is anticipated in achieving this result.

2.3 Phase III - Experimental Measurements

Several composites based on the Zr 28 raw materials have been machined into thermal conductivity specimens and measured during this quarter. In addition to the curves shown in figures 5, 10 and 12 of the attached paper, (converted into metric equivalents for the International Conference), a Thermal Conductivity vs. Temperature curve is attached for run No. 59.

This sample is a Zr 28 type matrix, impregnated after firing to a density of 0.6 g/cc with molybdenum metal by the solution metallizing technique. The multiple gauge section measurement again indicates a lower conductivity in the gauge section adjacent to the hot face which may be relatable to a decrease in photon conductivity. The curve of figure 12 of the attached paper is for a Zr 28 type matrix foamed with a 10 weight percent tungsten powder addition and fired in hydrogen to a 0.6 g/cc density. These data, in the metric system ($693.4^{W}/cm\text{-}^{o}C = 1\ BTU/hr/in/ft^{2}/^{o}F$), indicate the same reduction in photon conductivity in the hot face region.

A re-evaluation of the measurement apparatus was also completed during this quarter as described in the attached paper. Results indicate the multiple gauge section technique will be useful in determining the effect of the radiation attenuating phases being examined in the program.



X Gauge Section 1 — Adjacent to hot face

△ Gauge Section 2 — 1/8" to 1/4" from hot face

□ Gauge Section 3 — 1/4" to 3/8" from hot face

O Gauge Section 4 — 3/8" to 1/2" from hot face

THERMAL CONDUCTIVITY VS. TEMPERATURE
Run No. 59

3. PROGRAM FOR NEXT QUARTER

Fabrication of specimens of Zr 36 type zirconia foam containing the various thermal radiation barrier phases proposed will be continued. Specimens of comparable structure and density to the matrix Zr 36 material will be developed and produced.

Thermal conductivity data on both matrix Zr 36 specimens and similar material but containing the radiation barrier phases will be obtained.

A MULTIPLE GAUGE SECTION TECHNIQUE FOR THE MEASUREMENT OF THERMAL CONDUCTIVITY IN CERAMIC FOAM COMPOSITES TO 5000°F

- K. H. Styhr, National Beryllia Corp.

Many of you are familiar with the apparatus I'll be speaking about this morning and with the background of the program for which it was developed. For those of you who are not, I'll go over the general aspects of each before getting into recent developments, such as the multiple gauge section technique and some data on several ceramic and composite materials.

The National Beryllia Corporation is a high-temperature materials research and manufacturing company, specializing in the fabrication of oxide ceramics and more recently, in carbides, composites of ceramics, carbides and metals and in ceramic-metal assemblies. We are not specifically in the business of precise thermal and physical property measurement, except where utilized as a tool in the development of new concepts of ceramic materials. One program falling into this latter category is a research effort being conducted for the National Aeronautics and Space Administration of the United States on thermal insulation materials useful to hot-face temperatures of greater than 3000°F.

It is well known that low density foamed ceramic thermal insulation rapidly loses efficiency above 2400°F due to the transfer of heat through the pores by thermal radiation. The concept being investigated is the reduction of this radiation or photon contribution to the total or apparent thermal conductivity by the incorporation of a thermal radiation barrier phase into a low density foamed refractory structure. Mechanisms such as absorption and re-radiation by embedded particles, scattering by incorporated phases and reflection by metallic foil radiation barriers are being considered and evaluated.

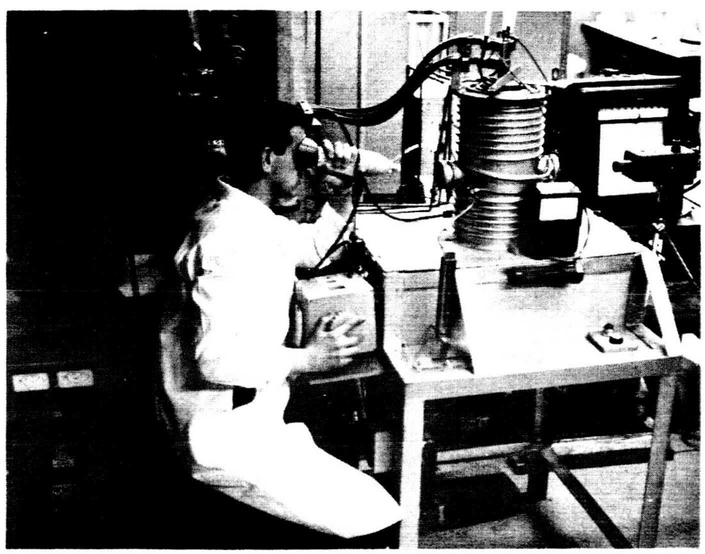
A necessary part of a materials development program such as this is an apparatus capable of comparing the heat transfer of one type of low thermal conductivity material with another in the high temperature range of interest. An expensive, elaborate apparatus was not justified on this program which requires only comparative data with reasonable reproducibility rather than absolute accuracy. Physical measurements and calculations should be simple and straight forward so that comparisons could be made by tecnicians rather than physicists.

The method selected was a steady state radial heat flow method employing a graphite hairpin heater internally in a hollow right circular cylindrical specimen. The intention is to dissipate all the heat from the electric heater uniformly within an infinitely long specimen cylinder. This heat dissipation ideally results in a radial temperature gradient with no longitudinal heat flow so that power input may be used as "Q" and only a measurement of the temperature gradient is required for the calculation of thermal conductivity. Longitudinal heat flow does, of course, exist as end losses are present. However, we felt we could minimize these by using a 9 inch high specimen stack and calculating conductivity in a small central region about one-twentieth of this height. Moreover, these losses would be essentially constant from one sample to the next and would therefore cancel in comparative data. If necessary, we felt we could standardize our apparatus by running a known or standard material and then applying a suitable correction factor to bring our measured values to within a few percent of a true value.

In initial experiments it was evident from isothermal color lines within the specimen that uniform radial heat flow conditions did exist in the central 7 to 8 inch region of the 9 inch high specimen. Also, measurements on specimens of dense zirconia, alumina, spinel and similar materials of known thermal properties agreed surprisingly well with measurements from more complex equipment in which "Q" was more precisely metered.

The apparatus is shown in figure 1 to give an idea of physical size and in figure 2 in cross-section to show internal construction. It is simply a cylindrical water-cooled steel shell 10" I.D. and 16 inches high. The graphite hairpin heater is suspended, by nickel terminals, from the top cover through a "Berlon" seal, one of the original applications of this new thermally conducting, electrically insulating, vacuum tight potting compound. The specimen, normally composed of three or more hollow 2 inch O.D. cylinders, fits snugly over the 3/4 inch O.D. graphite hairpin heater. Portions of the central 5 inch region of the specimen are visible through the three concentric molybdenum radiation shields, and the shell wall by means of 5 small molybdenum sight tubes at each of two fused quartz windows. It is by means of these sight tubes, aligned with holes drilled radially into the specimen to accurately known depths, that temperature gradient may be optically measured. The specimen stack is readily removeable from the bottom of the apparatus without disturbing the heater connections. The chamber is normally evacuated with a mechanical roughing pump and back filled with an inert gas to protect the graphite heater from oxidation.

Originally measurements were made only in one gauge section 3/8 inch long starting 1/8 inch from the hot face



THERMAL CONDUCTIVITY APPARATUS

Figure 1

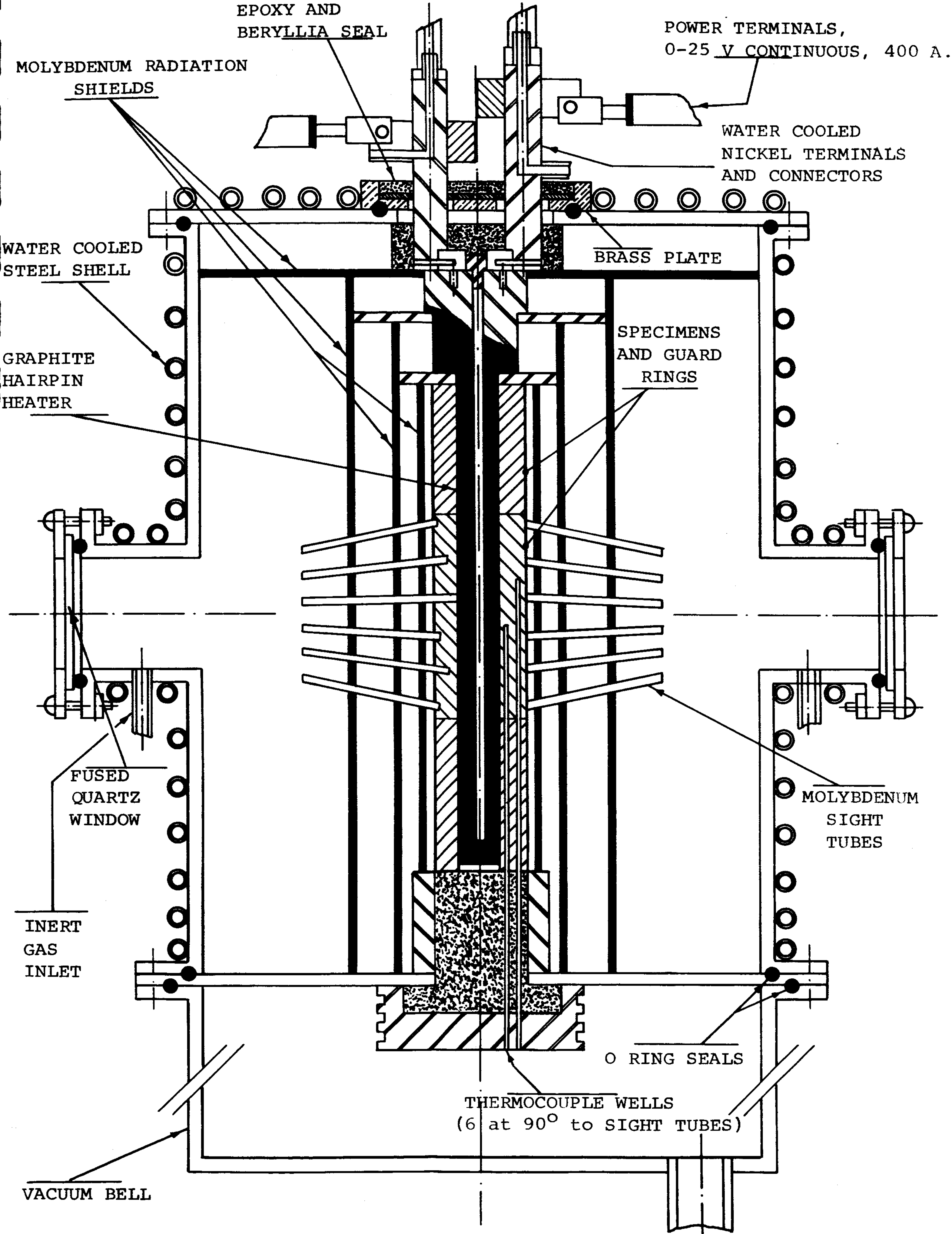
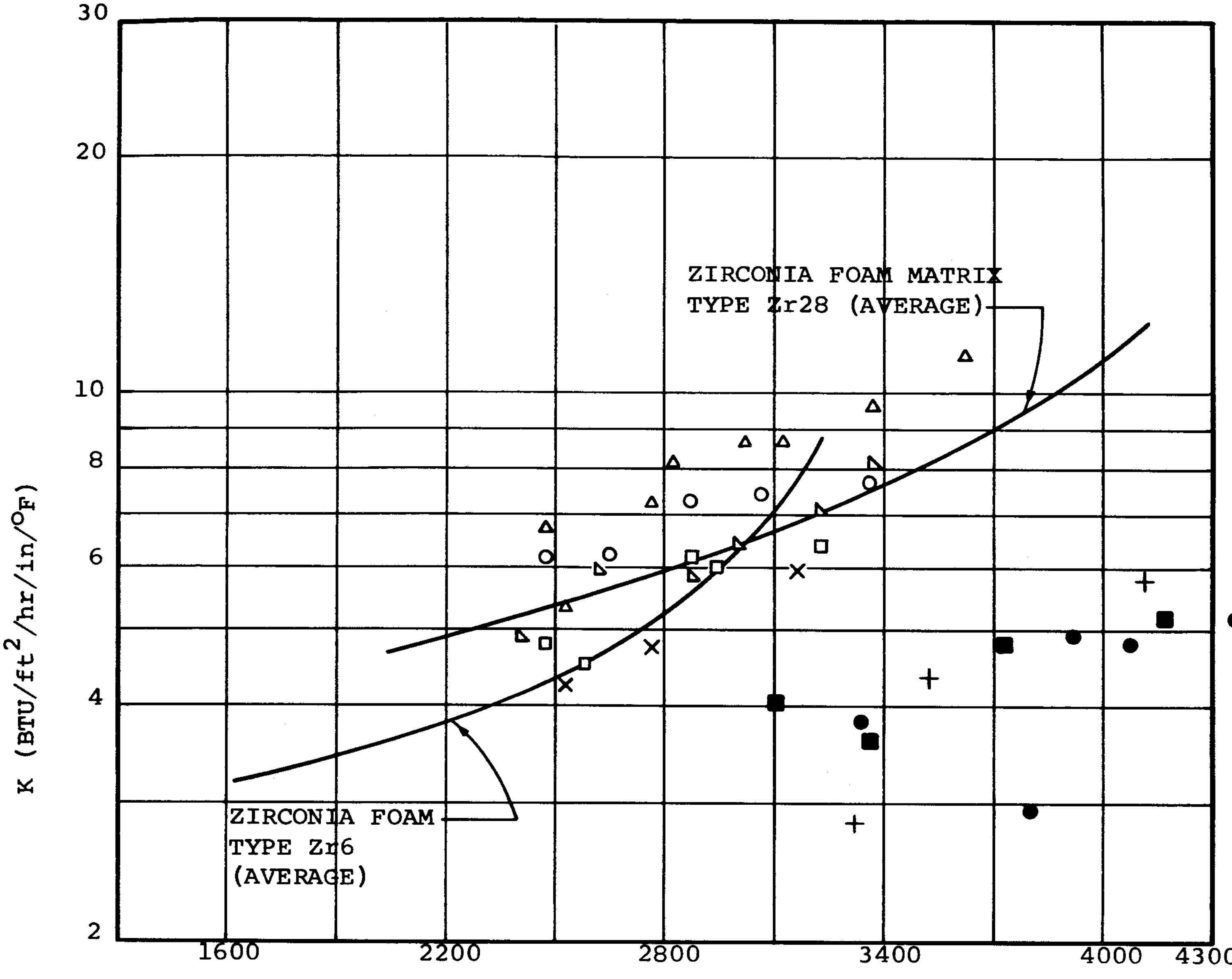

EPOXY AND
BERYLLIA SEAL
POWER TERMINALS,
0-25 V CONTINUOUS, 400 A.
MOLYBDENUM RADIATION
SHIELDS
WATER COOLED
NICKEL TERMINALS
AND CONNECTORS
WATER COOLED
STEEL SHELL
BRASS PLATE
SPECIMENS
AND GUARD
RINGS
GRAPHITE
HAIRPIN
HEATER
FUSED
QUARTZ
WINDOW
MOLYBDENUM
SIGHT
TUBES
INERT
GAS
INLET
O RING SEALS
THERMOCOUPLE WELLS
(6 at 90° to SIGHT TUBES)
VACUUM BELL

FIGURE 2

and extending outward to points 1/2 inch from the hot face. At least two sets of holes were measured from each sight window so that four temperature readings could be averaged for increased accuracy. The extreme temperature gradients possible in good thermal insulators, approaching 2000°C per inch, soon forced us to drill one or more through holes so that the heater temperature could be measured. This process yields a gauge section extending from the heater surface to a point 1/8 inch within the specimen. Data such as is shown in slide 3 resulted due not only to the different gauge lengths but the different emittance properties of graphite and ceramic foam and to the temperature drop between the heater and the inner surface of the specimen.

The next slide is a closeup showing how we have recently changed the sight holes' geometry. The uniformity of the heater temperature is monitored from one of the two fused quartz windows through three through holes having a maximum spread. The temperature gradient is measured from the opposite window by means of five molybdenum sight tubes, each positioned so that a sight hole drilled into the specimen at each of five different depths may be observed. Due to the porous nature of most of the foamed ceramic specimens being



Normal Inner Gage

△ —— Run 24, Zr28 with 10% tungsten flake

○ ● — Run 32, Zr28 with 20% tungsten flake

□ ■ — Run 26, Zr28 with 10% tungsten coated spheres

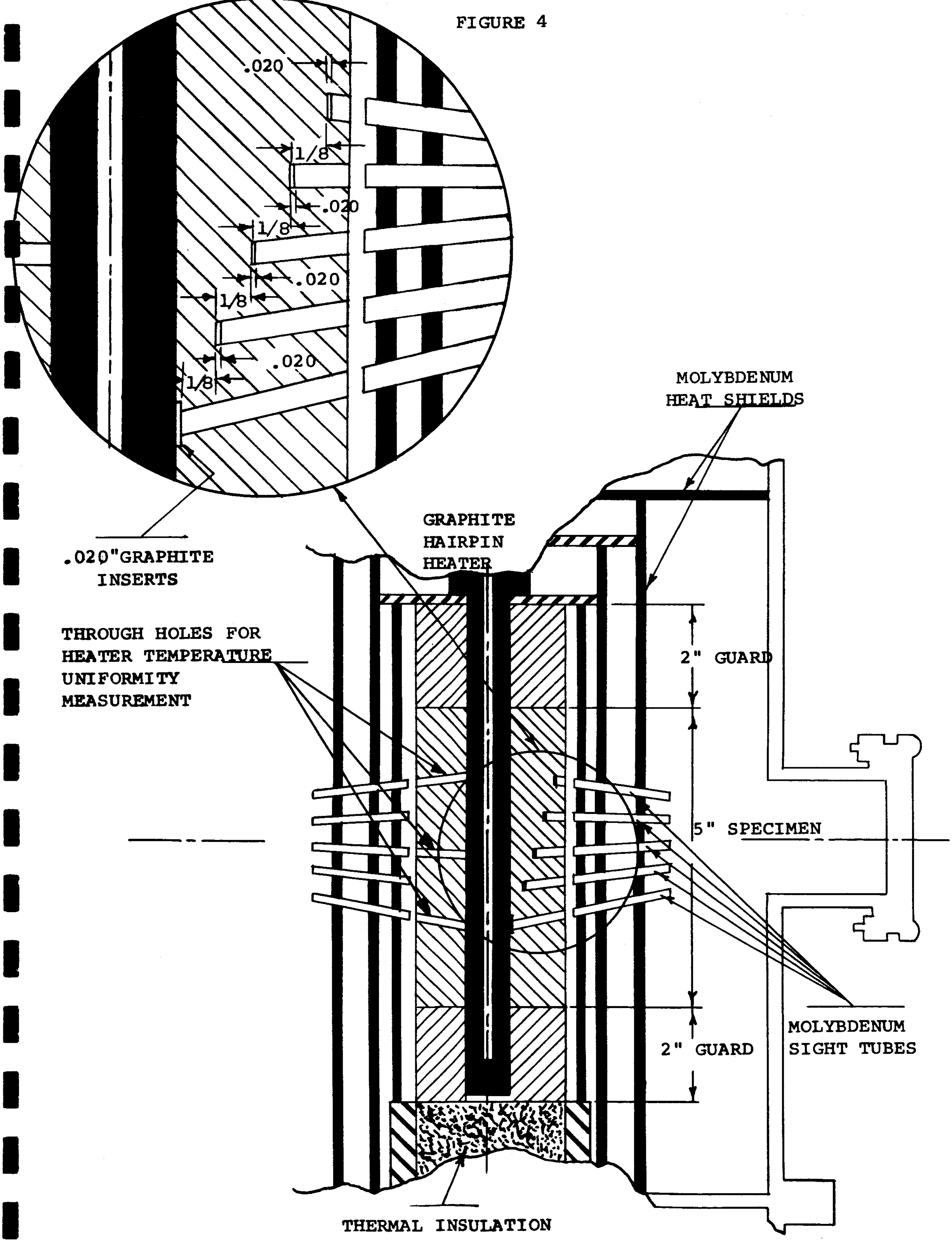
◺ — Run 30, Zr28 with 10% uncoated spheres

× + — Run 28, Zr28 with 10% Moly $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$

FIGURE 3

THERMAL CONDUCTIVITY VERSUS TEMPERATURE

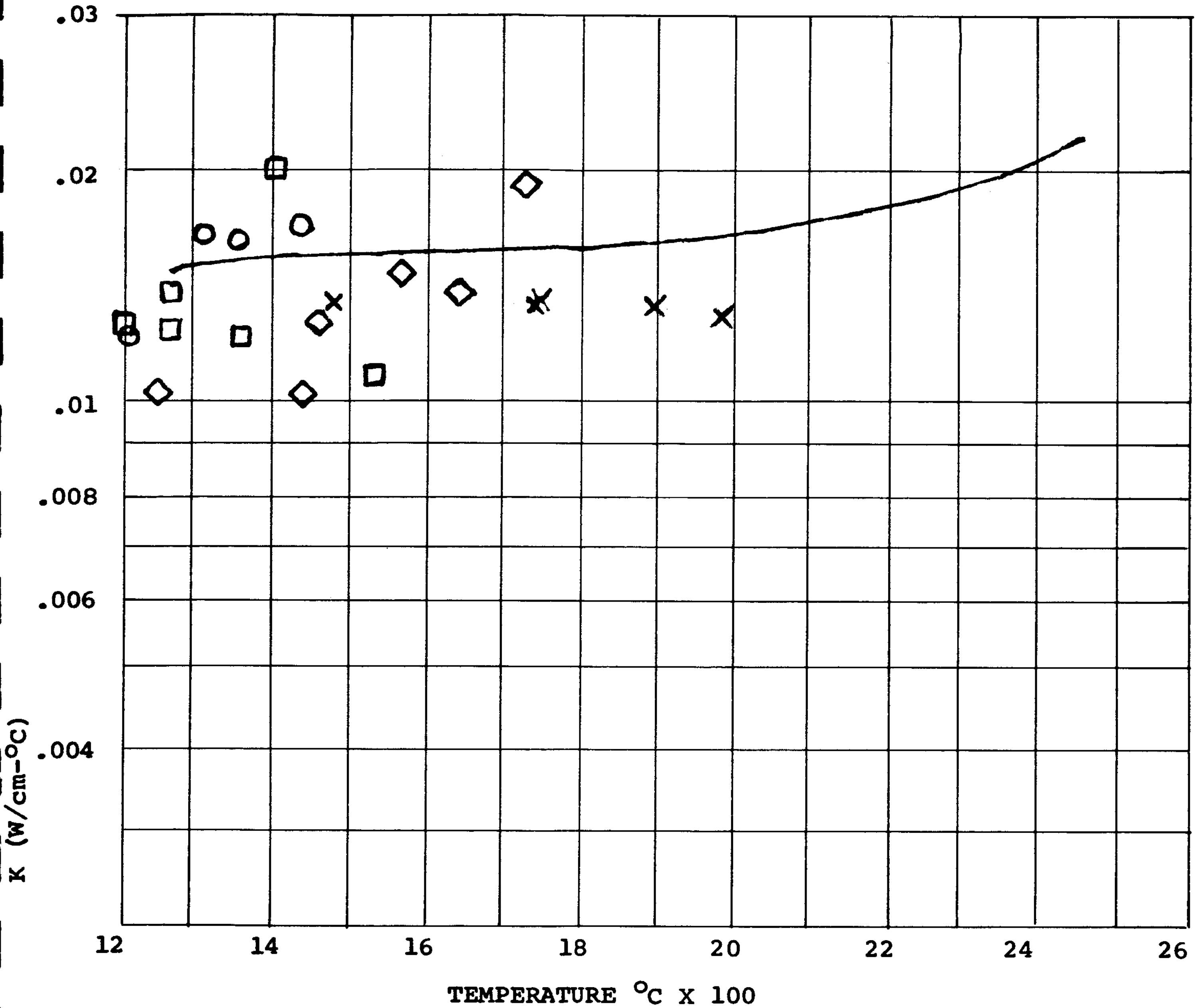
FIGURE 4



.020
1/8
.020
1/8
.020
1/8
.020
1/8
MOLYBDENUM HEAT SHIELDS
GRAPHITE HAIRPIN HEATER
.020"GRAPHITE INSERTS
THROUGH HOLES FOR HEATER TEMPERATURE UNIFORMITY MEASUREMENT
2" GUARD
5" SPECIMEN
2" GUARD
MOLYBDENUM SIGHT TUBES
THERMAL INSULATION

considered in this program, thin (0.020") graphite inserts are positioned snugly into the bottom of the flat bottom sight holes so that optical temperature measurements may be made on a graphite surface parallel to the isotherm in the specimen at a conveniently measurable radius. These graphite inserts materially affect the temperature measurement of the bottom of the sight hole but eliminate the non-uniform temperature gradient caused by the non-uniform, porous nature of the foamed ceramic sample. This procedure allows the calculation of four thermal conductivity values at four different temperatures at each steady state condition. Five steady state conditions, which normally constitute a 2-day run, allow the calculation of 20 overlapping values.

This multiple gauge section procedure was applied to a "dense" zirconia specimen obtained from Colt Pears of the Southern Research Institute, Birmingham, Ala., U.S.A. Two similar specimens were measured at S.R.I. on more elaborate equipment so that these measurements constitute somewhat of a "standardization" of the technique. The data are shown in slide 5. Considerable scatter is evident, however, no correction, averaging or other smoothing techniques have been applied. Rather, only raw data



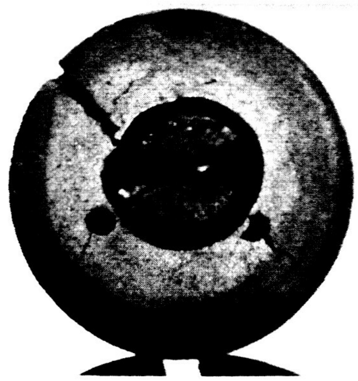
X-GAUGE SECTION 1 ADJACENT TO HOT FACE
◇-GAUGE SECTION 2 1/8" TO 1/4" FROM HOT FACE
□-GAUGE SECTION 3 1/4" TO 3/8" FROM HOT FACE
O-GAUGE SECTION 4 3/8" TO 1/2" FROM HOT FACE
——— SRI DATA ON "DENSE" ZrO_2

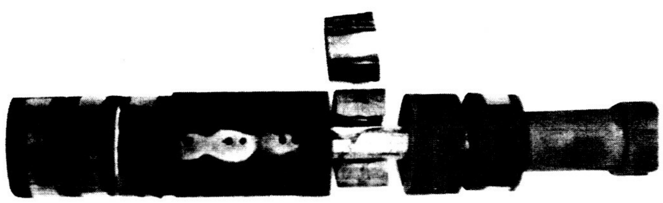
THERMAL CONDUCTIVITY VS. TEMPERATURE
DENSE ZIRCONIA SPECIMEN

Figure 5

points are shown. High temperature measurements are lacking due to a growth of fibers in the deep sight holes. These were shown to be the magnesium silicate compound Forsterite boiled out of a newly replaced graphite heater. Unfortunately, the temperature of the specimen was increased to the point where internal portions of the zirconia specimen were fused to the graphite heater. The next slide shows an overall view of the zirconia specimen and three 1 inch zirconia guard rings, all on the graphite hairpin heater. Evidence of the Fosterite whisker growth is evident at the sight hole positions. The isothermal color lines are evident in the fracture of the zirconia guard ring as is the fusion of the interior surface and a glazing of the graphite hairpin from molten zirconium oxide. Little evidence of zirconia carbide formation was found on the specimen, only on the graphite heater. Considerable zirconium metal was found on the specimens, however, due to reduction of the oxide by the graphite. The following slide is a longitudinal view of the S.R.I. zirconia specimen showing how the graphite hairpin heater is firmly embedded in the sample after cooling. The next slide is of a hairpin heater mounted on a brass plate in the Berlon seal showing how a heater looks without specimens fused around it.

The purpose of this program, of course, is to apply the



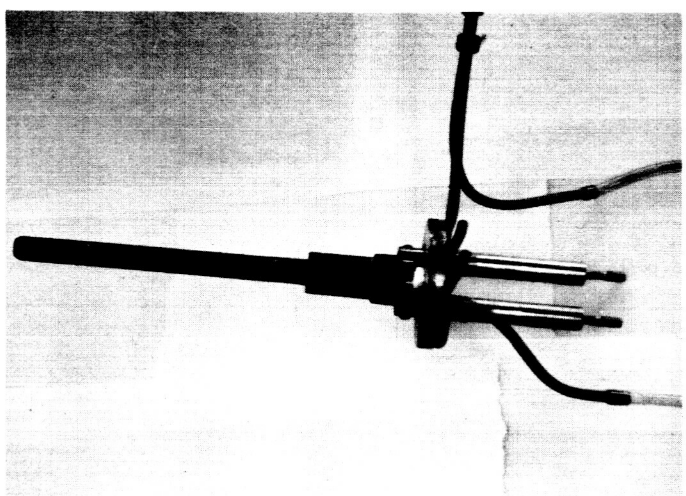


SRI ZIRCONIA SPECIMEN WITH

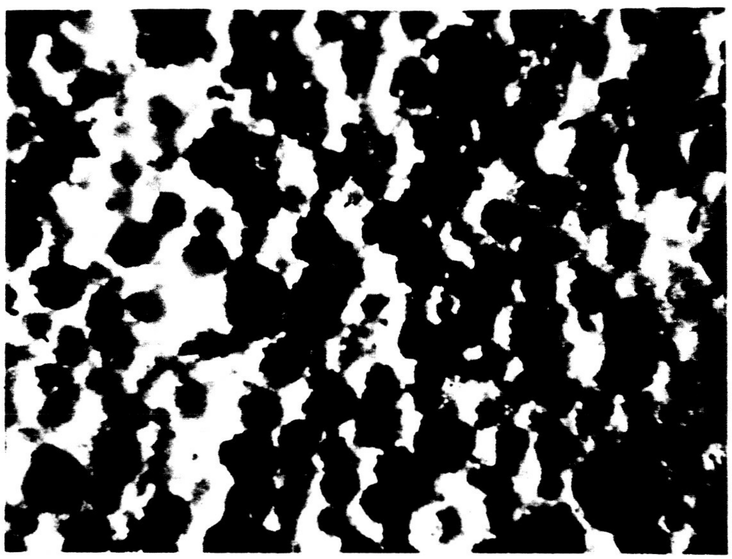
GUARD RINGS ON HEATER AFTER TEST

Figures 6 and 7

Figure 8



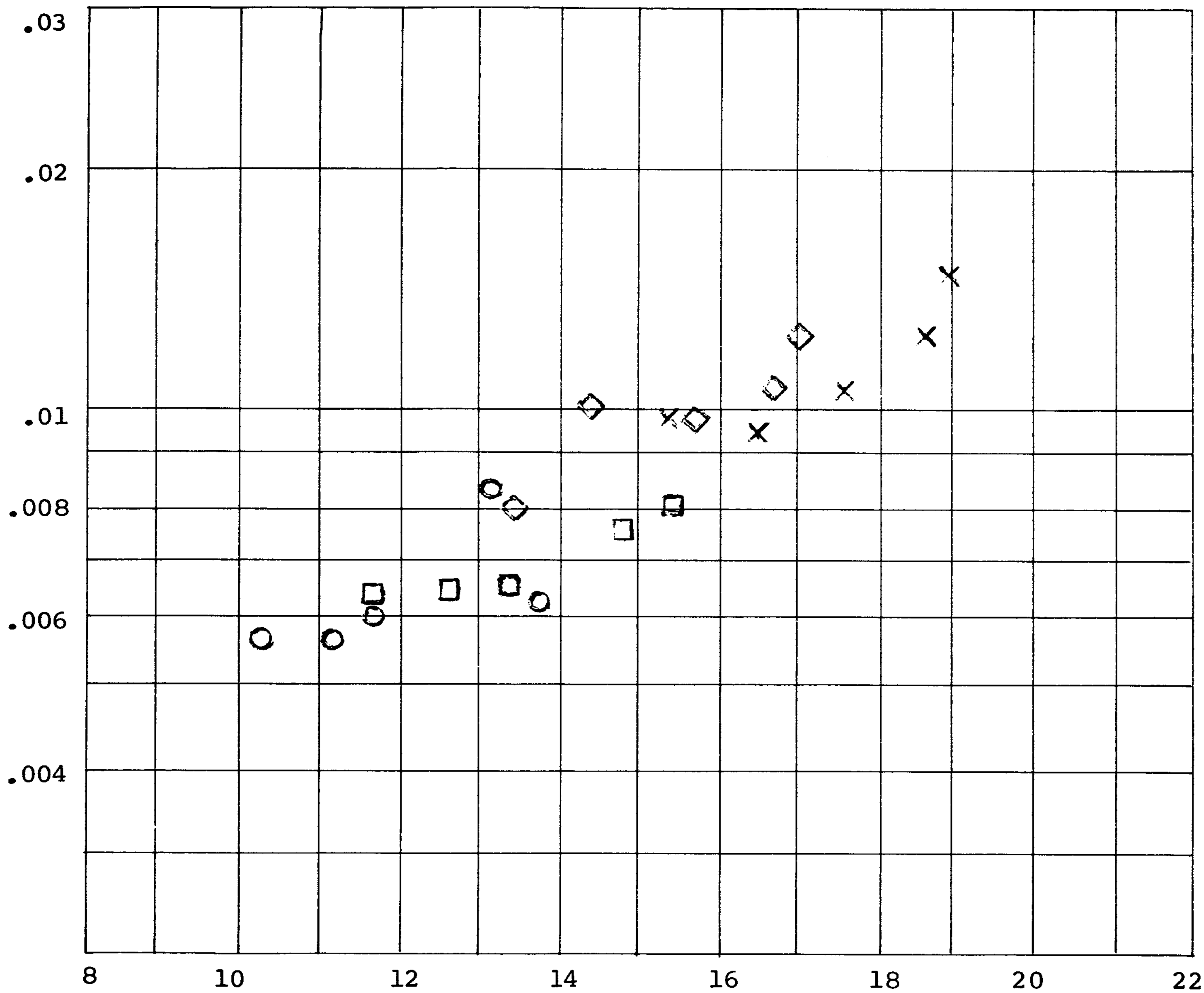
GRAPHITE HAIRPIN HEATER ASSEMBLY



100 μ

Figure 9

STABILIZED ZIRCONIA FOAM (50X)

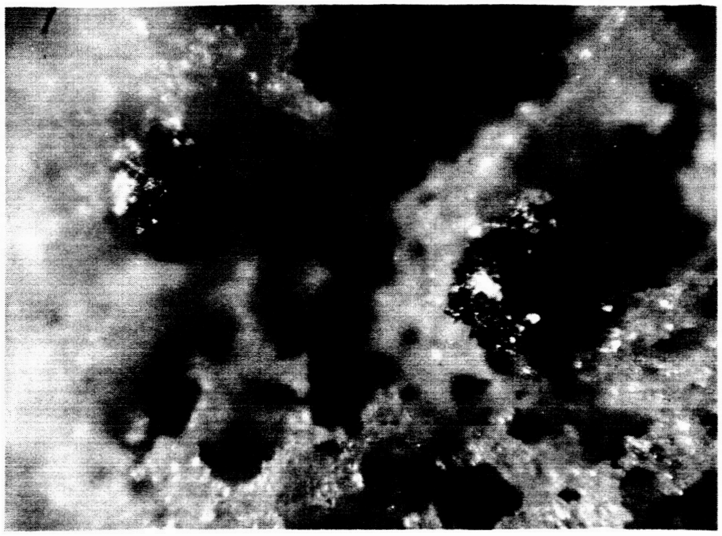


X - GAUGE SECTION 1 ADJACENT TO HOT FACE
◇ - GAUGE SECTION 2 1/8" TO 1/4" FROM HOT FACE
□ - GAUGE SECTION 3 1/4" TO 3/8" FROM HOT FACE
O - GAUGE SECTION 4 3/8" TO 1/2" FROM HOT FACE

THERMAL CONDUCTIVITY VS. TEMPERATURE

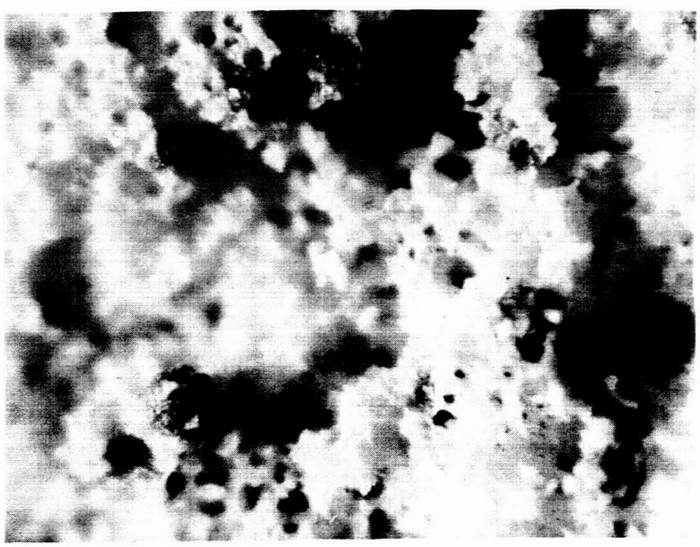
ZIRCONIA FOAM MATRIX

Figure 10



$\vdash\!\dashv$ 100 μ

ZIRCONIA FOAM WITH TUNGSTEN COATED HOLLOW ZIRCONIA MICROSPHERES (50X)



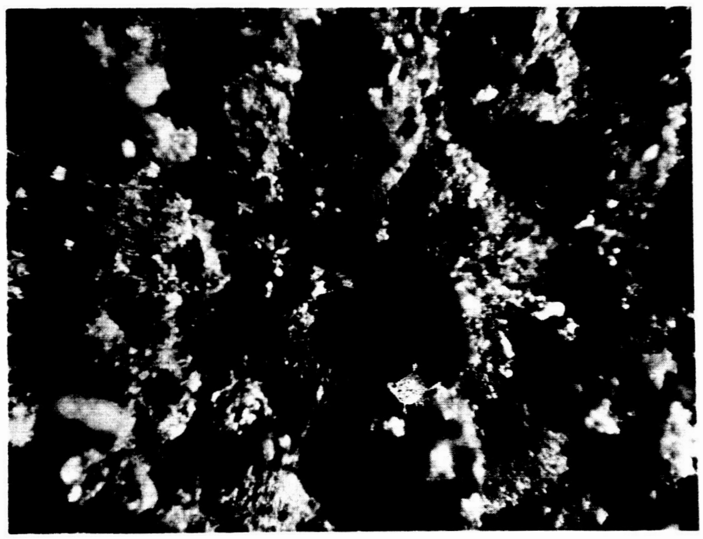
$\vdash\!\dashv$ 100 μ

ZIRCONIA FOAM WITH TUNGSTEN COATED HOLLOW ZIRCONIA MICROSPHERES (20X)

FIGURE 11

which then forms a non-continuous coating of molybdenum metal particles on all surfaces of the zirconia foam. Such a specimen, after firing, is shown in the next slide. Thermal conductivity measurements on specimens prepared in one of these latter methods is shown in the last slide. It is evident here that the conductivity in the gauge sections removed from the hot face is not affected particularly by the addition of the thermal radiation barrier phase. It is apparent, however, that in the areas immediately adjacent to the hot face the thermal conductivity values are definitely lower. I should point out that these data are very preliminary and that some specimens have been measured that do not show this type of thermal radiation attenuation in the areas adjacent to the hot face and that these data do require additional verification.

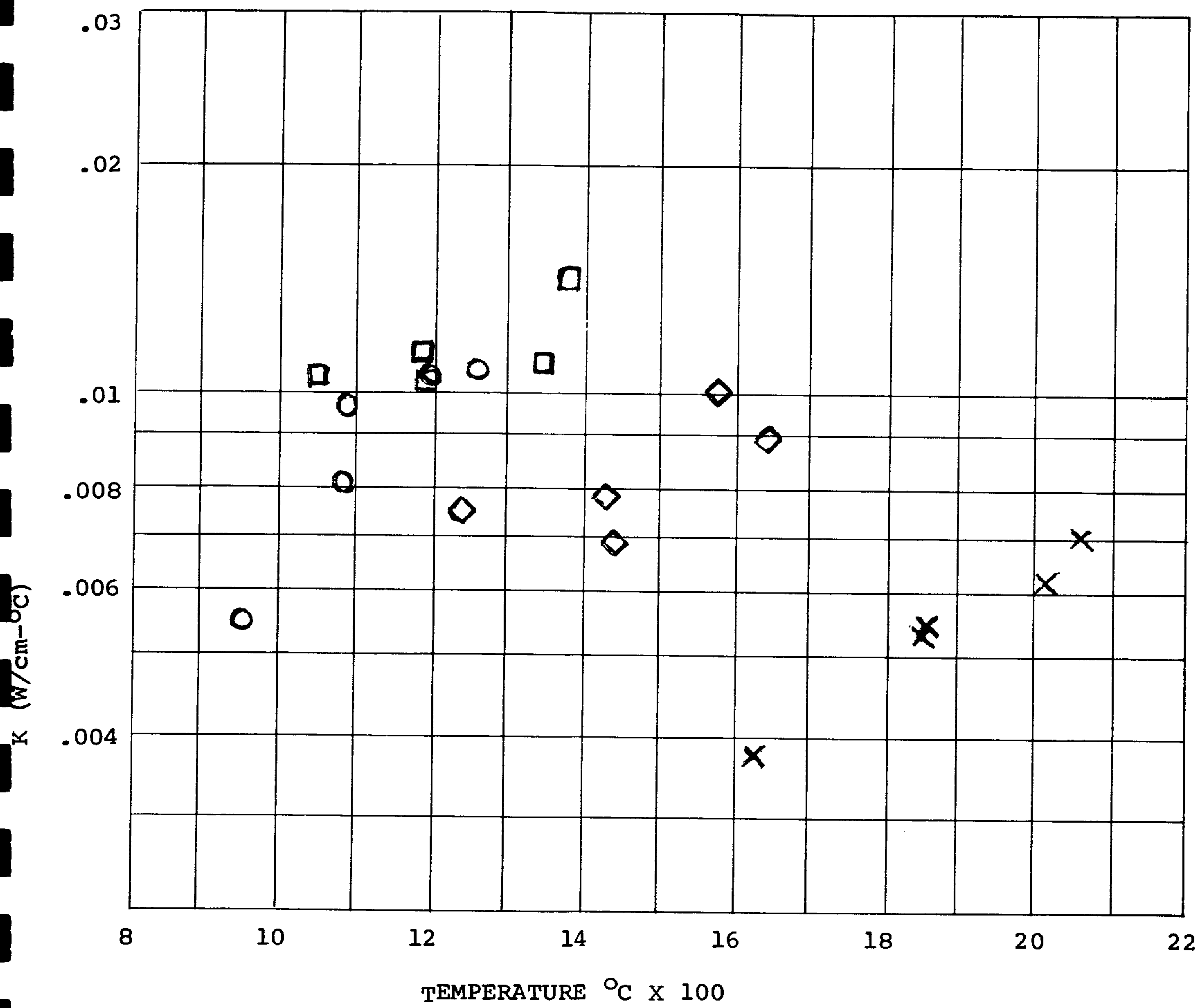
In conclusion, I would like to acknowledge the support of the National Aeronautics and Space Administration under Contract NASw 884 and the contributions of Dr. E. Ryshkewitch, P. S. Hessinger and other members of the National Beryllia Corporation research staff. We have developed what we feel is an inexpensive, simple, technique and analytical tool for the measurement of thermal conductivity of foamed ceramic specimens. I feel that the scatter in the data are reasonable



100 μ

ZIRCONIA FOAM WITH MOLYBDENUM METAL PARTICULATE COATING BY SOLUTION METALLIZING TECHNIQUE (50X)

FIGURE 2



✕ GAUGE SECTION 1 ADJACENT TO HOT FACE
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□ GAUGE SECTION 3 1/4" TO 3/8" FROM HOT FACE
○ GAUGE SECTION 4 3/8" TO 1/2" FROM HOT FACE

THERMAL CONDUCTIVITY VS. TEMPERATURE

ZIRCONIA FOAM-TUNGSTEN COMPOSITE

Figure 13

in light of the goals of the overall program and the degree of effort applied to this measurement technique. I would like now to solicit comments and a critique of the method and apparatus and possible suggestions as to how these determinations may be improved without any significant increase in the complexity of the cost.